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⑳ Fluorinated polyolefin membranes for aromatics/saturates separation.

㉑ Fluorinated polyolefin membranes are crosslinked by thermal treatment. An aromatics/saturates separation process employs a fluorinated polyolefin membrane which is pre-crosslinked, or becomes crosslinked in situ during the separation process.

The use of membranes to separate aromatics from saturates has long been pursued by the scientific and industrial community and is the subject of numerous patents.

U.S. Patent 3,370,102 describes a general process for separating a feed into a permeate stream and a retentate stream and utilizes a sweep liquid to remove the permeate from the face of the membrane to thereby maintain the concentration gradient drive force. The process can be used to separate a wide variety of mixtures including various petroleum fractions, naphthas, oils, hydrocarbon mixtures. Expressly recited is the separation of aromatics from kerosene.

U.S. Patent 2,958,656 teaches the separation of hydrocarbons by type, i.e., aromatic, unsaturated, and saturated, by permeating a portion of the mixture through a non-porous cellulose ether membrane and removing permeate from the permeate side of the membrane using a sweep gas or liquid. Feeds include hydrocarbon mixtures, e.g., naphtha (including virgin naphtha, naphtha from thermal or catalytic cracking, etc.).

U.S. Patent 2,930,754 teaches a method for separating hydrocarbons, e.g., aromatic and/or olefinic, from gasoline-boiling-range mixtures by the selective permeation of the aromatic through certain nonporous cellulose ester membranes. The permeated hydrocarbons are continuously removed from the permeate zone using a sweep gas or liquid.

U.S. Patent 4,115,465 teaches the use of polyurethane membranes to selectively separate aromatics from saturates via pervaporation. U.S. Patents 5,028,685 and 5,093,003 disclose halogenated polyurethanes and membranes therefrom for separating aromatics from saturates.

U.S. Patents 4,944,880 and 4,990,275 describe polyimide/ aliphatic polyester copolymers and membranes therefrom for the separation of aromatics from saturates. U.S. Patents 4,946,594 and 4,997,906 describe crosslinked copolymers of aliphatic polyester diols and dianhydrides and membranes therefrom for the separation of aromatics from saturates.

U.S. Patent 4,976,868 covers the use of polyester membranes (e.g., polyethylene terephthalate, polybutylene terephthalate, and polyethylene terephthalate/cyclohexane-dimethanol terephthalate) for aromatics/saturates separation. U.S. Patents 5,012,036, 5,012,035, and 5,019,666 teach the use of polyarylate, polyphthalatecarbonate, and nonporous polycarbonate membranes, respectively, to separate aromatics from saturates. U.S. Patent 5,055,631 discloses sulfonated polysulfone membranes for the separation of aromatics from saturates. U.S. Patent 5,128,439 describes saturated polyesters and crosslinked membranes therefrom for aromatics/saturates separation.

In 1973, F.P. McCandless (*Ind. Eng. Chem. Process Des. Develop.*, 12 (3), 354 (1973)) published a paper on the separation of aromatics from naphthenes by permeation through modified polyvinylidene fluoride membranes. The modifying agent was 3-methyl-sulfolane used as a plasticizer. The maximum temperature used by McCandless was 100°C. In practice, the membranes described by McCandless cannot have suitable stability; the plasticizer would be slowly leached out and contaminate the permeate, and the membrane performance would change with time.

In a subsequent paper, McCandless et al (*Ind. Eng. Chem. Process Des. Develop.*, 13 (3), 310 (1974)) investigated the separation of benzene from cyclohexane using a solvent-modified polyvinylidene fluoride film via adding the solvent in the hydrocarbon feed. The solvents were dimethylformamide (DMF) or dimethylsulfoxide. Such a solvent-modified membrane process cannot be practical in industrial use as it would require the separation of the solvent from the permeate and retentate.

The present invention describes a method to crosslink fluorinated polyolefin membranes by thermal treatment and the use of crosslinked fluorinated polyolefin membranes and uncrosslinked polyvinyl fluoride membranes for the separation of aromatics from saturates. As will result from the examples, the crosslinked membranes and uncrosslinked polyvinyl fluoride membranes covered by this invention can be used at temperatures well above those used by McCandless.

Compared to distillation, membrane permeation can lead to considerable energy savings. A membrane can separate a mixture of aromatics and saturates, e.g., a heavy catalytic naphtha, into a high-octane, mainly aromatic permeate and a high-cetane, mainly saturated retentate. Both permeate and retentate are more valuable than the starting heavy catalytic naphtha.

SUMMARY OF THE INVENTION

The present invention includes a method to crosslink fluorinated polyolefin membranes by thermal treatment and the use of crosslinked fluorinated polyolefin membranes and uncrosslinked polyvinyl fluoride membranes for the separation of aromatics from saturates.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The fluorinated polyolefins useful according to the present invention preferably melt below 250°C, more preferably below 200°C. Examples of homopolymers are polyvinylidene fluoride, polyvinyl fluoride, and polytrifluoroethylene. The present invention also covers the use of copolymers of fluorolefins with each other, e.g., vinylidene fluoride with hexafluoropropylene or copolymers with olefins, e.g., a nearly alternating copolymer of chlorotrifluoroethylene with ethylene available commercially under the name of Halar.

Membranes can be prepared by extrusion or by solution casting.

The thermal treatment to crosslink the membranes according to the present invention varies with the composition of the fluorinated polyolefin. As will result from the examples, heating a polyvinylidene fluoride membrane at 100°C and 150°C, each for 15 hours, leads to crosslinking. Other fluorinated polyolefins require higher temperatures and/or longer times.

Polyvinyl fluoride is insoluble in aromatics and saturates. Thus, uncrosslinked polyvinyl fluoride membranes can also be used for the separation of aromatics from saturates. As described in Example 5, a polyvinyl fluoride membrane can be crosslinked in situ, i.e., during use in a permeation experiment. Similarly, as described in Example 6, a polyvinylidene fluoride membrane can be crosslinked in situ.

The membranes are useful for the separation of aromatics from saturates in petroleum and chemical streams, and have been found to be particularly useful for the separation of large substituted aromatics from saturates as are encountered in heavy catalytic naphtha streams. Other streams which are also suitable feed streams for aromatics/saturates separation are intermediate catalytic naphtha streams boiling at 93°C-180°C, light aromatics content streams boiling in the 40°C-150°C range, light catalytic cycle oil boiling in the 200°C-345°C range jet fuel boiling in the 140°C-280°C range, diesel boiling in the 200°C-365°C range as well as streams in chemical plants which contain recoverable quantities of benzene, toluene, xylenes (BTX) or other aromatics in combination with saturates. Combinations of above streams are also suitable feed streams. The separation techniques which may successfully employ the membranes of the present invention include per-
traction and pervaporation.

Pertraction involves the selective dissolution of particular components contained in a mixture into the membrane, the diffusion of those components through the membrane, and the removal of the diffused components from the downstream side of the membrane by the use of a liquid sweep stream. In the pertractive separation of aromatics from saturates in petroleum or chemical streams, the aromatic molecules present in the feed stream dissolve into the membrane film more easily than the saturates, due to similarities between the membrane solubility parameter and those of the aromatic species in the feed. The aromatics then permeate (diffuse) through the membrane and are swept away by a sweep liquid which is low in aromatics content. This keeps the concentration of aromatics at the permeate side of the membrane film low and maintains the concentration gradient which is responsible for the permeation of the aromatics through the membrane.

The sweep liquid is low in aromatics content so as not to itself decrease the concentration gradient. The sweep liquid is preferably a saturated hydrocarbon liquid with a boiling point much lower or much higher than that of the permeated aromatics. This is to facilitate separation, as by simple distillation. Suitable sweep liquids, therefore, would include, for example, C₃ to C₆ saturated hydrocarbons and lube base stocks (C₁₅-C₂₀).

The pertraction process is run at any convenient temperature, preferably as low as possible.

The choice of pressure is not critical since the pertraction process is not dependent on pressure, but on the ability of the aromatic components in the feed to dissolve into and migrate through the membrane under a concentration driving force. Consequently, any convenient pressure may be employed, the lower the better to avoid undesirable compaction, if the membrane is supported on a porous backing, or rupture of the membrane, if it is not. If C₃ or C₄ sweep liquids are used at 25°C or above in liquid state, the pressure must be increased to keep them in the liquid phase.

Pervaporation, by comparison, is run at generally higher temperatures than pertraction and relies on vacuum on the permeate side to evaporate the permeate from the surface of the membrane and maintain the concentration gradient driving force which drives the separation process. As in pertraction, the aromatic molecules present in the feed dissolve into the membrane film, migrate through said film and emerge on the permeate side under the influence of a concentration gradient. Pervaporation separation of aromatics from saturates can be performed at a temperature of about 25°C for the separation of benzene from hexane but for separation of heavier aromatic/saturate mixtures, such as heavy catalytic naphtha, higher temperatures of at least 80°C and higher, preferably at least 100°C and higher, more preferably at least 120°C have been successfully used with membranes prepared from fluorinated polyolefins, the maximum upper limit being that temperature at which the membrane is physically damaged. Vacuum on the order of 1-80 mm Hg is pulled on the permeate side. The vacuum stream containing the permeate is cooled to condense out the highly aromatic permeate. Condensation temperature should be below the dew point of the permeate at a given vacuum level.

Instead of a vacuum, a sweep gas may also be used in the permeate side.

The membrane itself may be in any convenient form utilizing any convenient module design. Thus, sheets of membrane material may be used in spiral-wound or plate-and-frame permeation cell modules. Tubes and hollow fibers of membranes may be used in bundled configurations with either the feed or the sweep liquid (or vacuum) in the internal space of the tube or fiber, the other material obviously being on the other side.

When the membrane is used in a hollow fiber configuration with the feed introduced on the exterior side of the fiber, the sweep liquid flows on the inside of the hollow fiber to sweep away the permeated highly aromatic species, thereby maintaining the desired concentration gradient. The sweep liquid, along with the aromatics contained therein, is passed to separation means, typically distillation means, however, if a sweep liquid of low enough molecular weight is used, such as liquefied propane or butane, the sweep liquid can be permitted to simply evaporate, the liquid aromatics being recovered and the gaseous propane or butane (for example) being recovered and reliquefied by application of pressure or lowering of temperature.

The membranes are used to separate aromatics from saturates in a pervaporation apparatus. The pervaporation apparatus is a cell, separated into two compartments by a porous metal plate, on which the membrane is supported. During a pervaporation experiment the aromatics/saturates mixture is circulated through the upper compartment at the desired temperature. The lower compartment is kept at atmospheric pressure and swept with a slow stream of inert gas, e.g., argon, which carries the permeate to a gas chromatograph for analysis. Otherwise, the lower compartment is kept under vacuum and the permeate goes directly to a mass spectrometer for analysis or is condensed in a trap and then analyzed by gas chromatography. In our experiments the feed is a toluene/n-octane mixture containing the two hydrocarbons in approximately equal weights.

The following examples illustrate the invention without limiting it.

Example 1

20 g of polyvinylidene fluoride known under the commercial name of Kynar 461 was dissolved in 85 g of dimethylformamide (DMF). The thick solution so obtained was cast on a Gore-Tex^R (porous Teflon) support. After most of the DMF had evaporated, a membrane was heated at 100°C and 150°C, each time for 15 hours, which led to insolubility in DMF, i.e., crosslinking.

A piece of membrane was tested in the pervaporation apparatus described above with the permeate side kept under vacuum, using a feed consisting of equal weights of toluene and n-octane. Analyses of the permeates were carried out by mass spectroscopy. The following table gives the results:

T(°C)	Toluene/n-Octane Separation Factor	Normalized Flux (Permeability) (Kg•μM/M ² •D)
150	8.3	523
170	6.1	4028
190	5.1	6480
210	4.5	9720

In this table, the separation factor is defined as the ratio of toluene and n-octane concentrations in the permeate divided by the ratio of toluene and n-octane concentrations in the feed. The normalized flux, i.e., permeability, is expressed in the unit of kilogram of the permeate per meter square membrane area per day for a normalized membrane thickness of 1 micron (Kg•μM/M²•D).

Example 2

A polyvinylidene fluoride membrane was prepared and crosslinked as described in Example 1. In the permeator, the permeate side was kept at atmospheric pressure and swept with a slow stream of argon, which carried the permeate to a gas chromatograph. The following table gives the results:

T(°C)	Toluene/n-Octane Separation Factor	Normalized Flux (Permeability) (Kg•μM/M ² •D)
150	8.7	1,200
170	6	6,500
190	5.1	9,600
210	4.8	13,000
225	4	18,000

Example 3

A copolymer of 65 wt% vinylidene fluoride and 35 wt% hexafluoropropylene, commercially known as Tecnoflon, was dissolved in dimethylformamide and a membrane was cast on a Gore-Tex^R support. The membrane was crosslinked by heating it as indicated below:

T(°C)	Hours
100	16
150	17
200	16.5
250	33
300	30
320	30

The membrane so treated became insoluble in dimethylformamide, i.e., crosslinked. It was tested in the apparatus described in Example 2. The following table gives the results:

T(°C)	Toluene/n-Octane Separation Factor	Normalized Flux (Permeability) (Kg•μM/M ² •D)
150	3.2	1,500
167	2.3	1,500
187	2.1	2,300
195	2.0	2,600
215	1.9	5,600

Example 4

A 2-mil-thick film of polyvinyl fluoride was heated at 100°C and 150°C, each time for 15 hours, then tested in the apparatus described in Example 2. The following table gives the results:

T(°C)	Toluene/n-Octane Separation Factor	Normalized Flux (Permeability) (Kg•μM/M ² •D)
150	8.6	620
165	7.3	2,020
180	6.2	5,300
210	5.4	9,760
230	4.6	12,408
262	3.8	19,300

Example 5

Polyvinylfluoride, as supplied, is soluble in dimethylformamide (DMF) at 110°C.

However, polyvinylfluoride heated at 100°C for 15 hours and at 150°C for another 15 hours is insoluble in DMF at 110°C.

Furthermore, a polyvinylfluoride membrane becomes insoluble in DMF at 110°C after use showing that it became cross-linked in situ.

Example 6

A 2 mil thick polyvinylidene fluoride film prepared by extrusion was tested in the permeator described in Example 2. The temperature was maintained at 150°C for 39 hours to give the membrane enough time to cross-link in situ. The following table gives the results:

T (°C)	Toluene/n-Octane Separation Factor	Normalized Flux (Permeability) (Kg•μM/M ² •D)
150	7.2	600
160	6.3	1,500
170	5.7	2,400
180	5.3	3,300
190	5.0	4,000
200	4.5	4,300
210	4.3	20,000

The used membrane was insoluble in dimethylformamide, i.e., it had undergone crosslinking in situ.

Claims

1. A process to crosslink fluorinated polyolefin membranes comprising heating a fluorinated polyolefin membrane at a temperature of at least about 100°C for a time to crosslink said membrane.
2. A process according to claim 1, wherein said fluorinated polyolefin is a homopolymer, a copolymer of two fluorinated olefins with each other or a copolymer of a fluorinated olefin with an olefin.
3. A process according to claim 2, wherein said homopolymer is polyvinylidene fluoride, polyvinylfluoride, or polytrifluoroethylene.
4. A process according to claim 2, wherein said copolymer is a vinylidene fluoride-hexafluoropropylene copolymer or is an alternating copolymer of ethylene and chlorotrifluoroethylene.

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6. A process for the separation of mixtures of aromatics and saturates into aromatics-enriched and saturates-enriched streams, comprising
- a) contacting said aromatics/saturates mixture with one side of a polyfluoroolefin membrane which is crosslinked or is crosslinkable in situ in said separation process.
- and
- b) selectively permeating the aromatic components of the mixture through the membrane.
- 10
7. A process according to claim 6, wherein said fluorinated polyolefin membrane is crosslinked by heating above about 100°C prior to said contacting step or during said contacting step with in situ crosslinking.
8. A process according to claim 6 or claim 7, wherein said fluorinated polyolefin is a homopolymer, a copolymer of two fluorinated olefins with each other or a copolymer of a fluorinated olefin with an olefin.
- 15
9. A process according to claim 8 wherein said homopolymer is polyvinylidene fluoride, polyvinyl fluoride, or polytrifluoroethylene.
- 20
10. A process according to claim 8 wherein said copolymer is a vinylidene fluoride-hexafluoropropylene copolymer or is an alternating copolymer of ethylene and chlorotrifluoroethylene.
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